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Photochemically Generated Bicyclic *ortho*-Quinodimethanes: Photo-enolization of Bicyclic Aldehydes and Ketones

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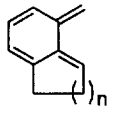
Abstract: A photoenolization route to bicyclic *ortho*-quinodimethanes was investigated. Bicyclic photoenols were trapped in an intermolecular fashion with various dienophiles for the first time. All *ortho*-quinodimethane precursors were prepared via a selective route commencing with 1-indanol, α-tetralol and 1-benzosuberone. Irradiation afforded the *E*-photoenols exclusively which were trapped with equal efficiency except that derived from indane-4-carboxaldehyde. This low efficiency has been ascribed to rapid auto-oxidation of the aldehyde to carboxylic acid. The facial selectivity of the reaction between the photoenol from benzosuberan-9-carboxaldehyde and dimethyl fumarate was much lower when compared to the other aldehydes in this study. A distorted diene caused by the presence of the seven membered ring explains these results. © 1997 Elsevier Science Ltd.

The photochemistry of *ortho*-alkyl benzaldehyde and related carbonyl compounds has seen explosive growth since Yang reported the successful photoenolization of *ortho*-methyl and -benzyl benzophenone.[1,2] The mechanism of this photo-enolization is now very well understood, and many of the intermediates have been observed and characterized *via* time resolved spectroscopy.[3] The seminal work of Sammes is largely responsible for inspiring the impressive amount of work that has been reported in the area of *ortho*-quinodimethane and benzocyclobutanol chemistry.[4-6]

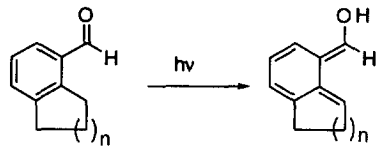
For quite some time, we have been interested in the area of photoenolization, especially as it relates to the synthesis of sulfones and sultines.[7-10] Quite recently we have become interested in the study of bicyclic *ortho*-quinodimethanes (**1**).[11] Given the amount of chemistry done in this area, it is remarkable that these compounds have not been studied.



1; n=1-3

We recently reported the first successful preparation of these short-lived intermediates from tricyclic sulfones via chelotropic expulsion of SO_2.[11] Continuing our research in this area, we have now investigated a photoenolization strategy as shown below (Scheme 1). Although 5,8-dimethyl-1-tetralone has been photoenolized, only the *Z*-enol is formed thus trapping with dienophiles in not possible since the lifetime of the intermediate is too short.[3,12-14] We have prepared a series of carbonyl compounds that affords the longer-lived *E*-photoenol when irradiated. The steady-state reactions of these photoenols with various dienophiles is the subject of this paper.

Scheme 1

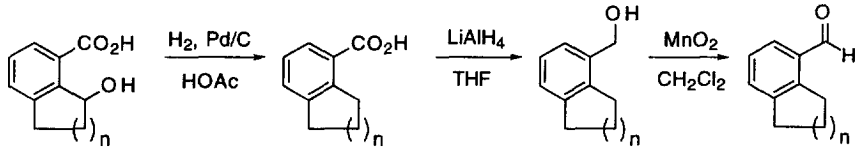


2; n=1
3; n=2
4; n=3

5; n=1
6; n=2
7; n=3

Wightman has previously prepared aldehydes **2** to **4**,[15] but the synthesis was not regioselective, making it necessary to carry isomers through a number of steps. In order to circumvent these problems, we utilized another strategy (Scheme 2).

Scheme 2



8; n=1
9; n=2

10; n=1
11; n=2

12; n=1
13; n=2

2; n=1
3; n=2

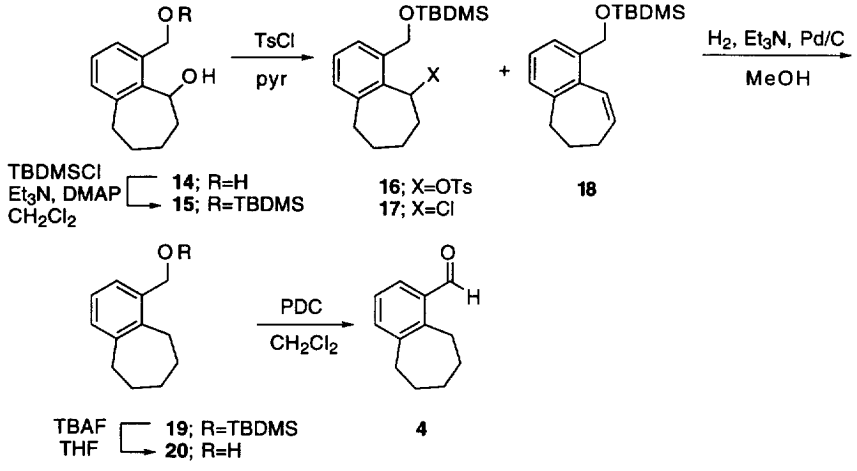
Hydrogenolysis of hydroxy-acids **8-9**, obtained as previously described,[11] was best accomplished using a catalytic amount of 10% Pd/C in glacial acetic acid, which gave acids **10** and **11** in yields of 90% and 75% respectively. Although hydrogenolysis could be achieved using a catalytic amount of hydrochloric acid in methanol, significant esterification of acids **10-11** occurred, making it difficult to assay purity. The acids formed using glacial acetic acid as the solvent were highly crystalline and readily purified by recrystallization. Conversion of the acid group to the aldehyde using a two-step procedure involving lithium aluminium hydride reduction and subsequent oxidation of the benzylic alcohol to the aldehyde with manganese dioxide in methylene chloride afforded aldehydes **2** and **3** as clear oils in yields of 84 and 68% from acids **10** and **11** respectively after elution through a plug of silica gel.

The procedure described above for the preparation of aldehydes **2** and **3** did not lend itself to the preparation of the benzosuberane derived aldehyde **4**. Although benzosuberanol could be *ortho*-metallated and quenched with carbon dioxide, the product that resulted was a lactone. In our hands, this lactone could not be converted to the desired hydroxy-acid, thereby eliminating the possibility of hydrogenolysis. This lactonization, although interesting in the context of other substrates,[11] proved troublesome towards the synthesis of **4**. In order to prepare the desired target, it was necessary to use a longer sequence (Scheme 3).

Protection of the primary hydroxyl group of **14** as a *t*-butyldimethylsilyl ether with *t*-butyldimethylsilyl chloride and triethylamine in methylene chloride containing a catalytic amount of 4-(dimethylamino)pyridine proceeded in >95% yield. Activation of the secondary hydroxyl group of **15** with *p*-toluenesulfonyl chloride led to a mixture of tosylate **16**, chloride **17** and alkene **18**. Hydrogenation of this mixture with 10% Pd/C in methanol led to the ether **19** in a yield of 83% provided that triethylamine was added to the solution prior to the

introduction of hydrogen. In the absence of added base, hydrogenolyis of the carbon-chlorine bond of **17** was very rapid, leading to the generation of hydrogen chloride which facilitated hydrogenolysis of the benzylic ether. Reaction of **15** with *p*-toluenesulfonic anhydride in pyridine avoided these problems, leading smoothly to alkene **18** which was readily hydrogenated to ether **19** by bubbling hydrogen through a methanolic solution of **18** containing palladium on carbon. Average overall yields for the conversion of **15** to **19** were about 70%. Desilylation of ether **19** with tetrabutylammonium fluoride afforded alcohol **20** (85% yield) which was smoothly converted to aldehyde **4** via oxidation with pyridinium dichromate in methylene chloride in 80% yield.

Scheme 3



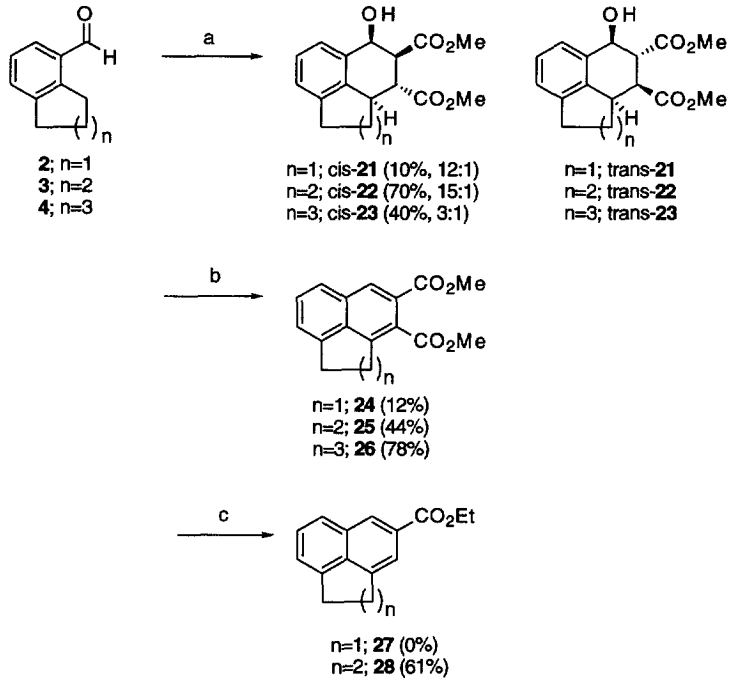
With the desired aldehydes in hand, their steady-state photochemistry was examined. All reactions were conducted in deaerated acetonitrile, in pyrex reaction vessels, using a medium pressure mercury arc lamp as a light source. The results of reactions with typical dienophiles are summarized in Scheme 4.

Examination of the trapping results shows that aldehydes **3** and **4** reacted with standard dienophiles in moderate to good yields. Reaction with dimethyl fumarate provided two isomers from endo and exo addition of the dienophile to the intermediate photoenol. It is not possible to assign the cyclodducts as endo or exo products when using a trans substituted dienophile, since one of the ester groups will always be endo. For this reason, the cycloadducts are referred to as cis and trans, reflecting the relative stereochemistry of the carbinol proton and the adjacent methine proton. These isomers were readily identified by the size of the coupling constant between these two protons. The benzylic methine proton resonated around 5 ppm, and typically displayed a 3 Hz coupling constant for the cis cycloadduct wheras the trans adduct had a 10 Hz coupling constant. Although comparable for aldehydes **2** and **3**, the selectivity was much lower for aldehyde **4**. Since endo/exo selectivity is controlled by secondary orbital interactions, we evaluated the HOMOs of the intermediate photoenols **5-7**.

PM3 calculations have shown that the coefficients of the HOMOs of **5-7** are independent of ring size (Figure 1). However, inspection of the minimized geometry of **5-7** points out that photoenol **7** is quite distorted. The seven membered ring causes the diene to deviate from the planar comformation adopted by dienes **5** and **6**. This is evident by the large difference in the dihedral angle between the arms of the dienophile for enols **5** and **6**, which have dihedral angles of essentially zero, versus enol **7**, for which the dihedral angle is

almost 40 degrees. Additionally, the seven membered ring is quite puckered. This distortion of the diene or the deviation from planarity, both of which are imposed by the presence of the seven membered ring, may account for the lower facial selectivity observed in the reaction of **7** with dimethyl fumarate. These distortions are apparent in the PM3 minimized structure of enol **7** (Figure 2). The effects of distorted diene geometry on facial selectivity are well documented.[16]

Scheme 4



Reagents: a) Dimethyl Fumarate, MeCN, hν. b) (i) Dimethyl acetylenedicarboxylate, MeCN, hν; (ii) TsOH. c) (i) Ethyl propiolate, MeCN, hν; (ii) TsOH.

Figure 1 PM3 Calculated HOMO's for Photoenols **5-7**

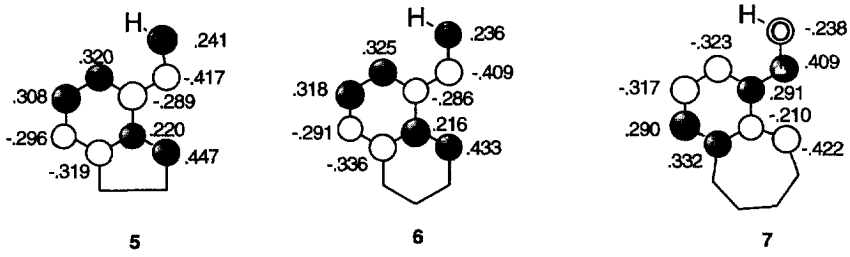


Figure 2 Front and Side View of PM3 Minimized Geometry of Photoenol **7**. The hydrogens are omitted for clarity in the side view.

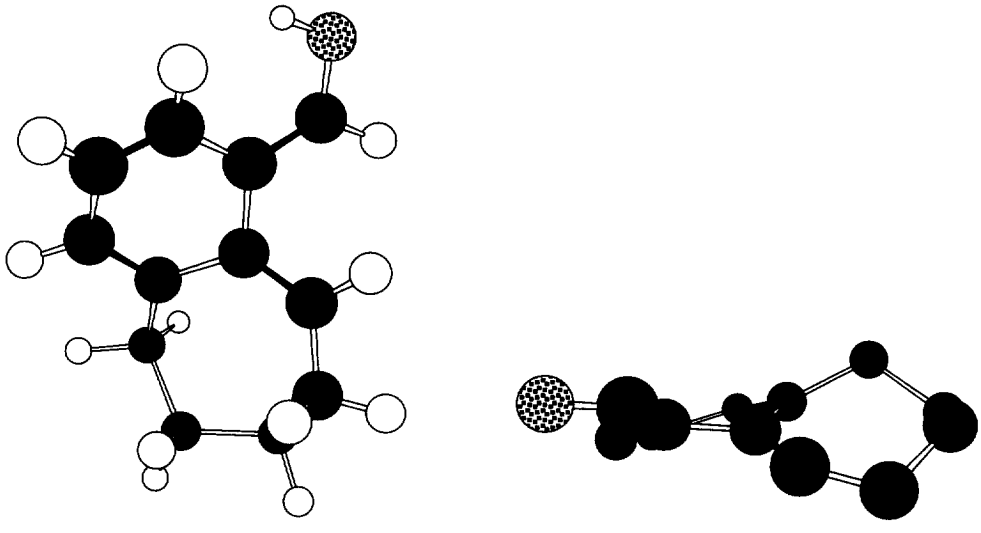


Table 1 Summary of PM3 Results for Photoenols **5-7**

	Photoenol **5**	Photoenol **6**	Photoenol **7**	*o*-tolualdehyde[d]
C-C Distance[a]	3.04 Å	2.86 Å	2.96 Å	2.86 Å
H-H Distance[b]	2.38 Å	1.85 Å	2.31 Å	1.89 Å
Dihedral Angle[c]	0 °	2.6 °	39.87 °	0 °

[a] Refers to intramolecular distance between the two terminal carbons of the diene.

[b] Refers to the intramolecular distance between the two hydrogens on the terminal carbons of the diene.

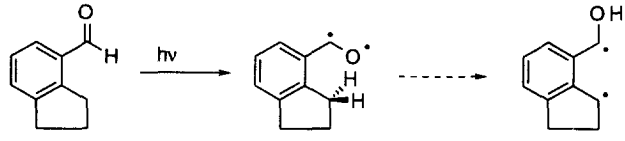
[c] Refers to the angle between the two terminal olefins of the diene.

[d] Calculations performed on the photoenol derived from *o*-tolualdehyde, to be used as a standard.

Reaction of the photoenols from **2-4** with dimethylacetylene dicarboxylate (DMAD) led to dihydronaphthols which were aromatized prior to isolation. Aldehydes **3** and **4** afforded naphthalenes **25** and **26** in yields of 44 and 78% respectively. As expected, reaction of the photoenol from **3** with ethyl propiolate led to only one regioisomer. The intermediate dihydronaphthol was also converted to the naphthalene derivative **28** to simplify product isolation and identification. The regiochemistry was confirmed by the presence of two lowfield doublets at 7.80 and 8.40 ppm with coupling constants of 1 Hz. These resonances were assigned to the isolated aromatic protons which flanked the carboethoxy group of the B aromatic ring.

Contrary to the observed reactivity of **3** and **4**, aldehyde **2** reacted only with very reactive dienophiles and even then, only sparingly. No reaction occurred with ethyl propiolate. Because of the low yields, cycloadducts **21** and **24** could not be isolated in significant enough amounts to allow for a full spectral

characterization. One possible explanation for this behavior is a geometry limitation imposed by the five membered ring. If the triplet **29** cannot attain the correct geometry to abstract a γ-hydrogen, then conversion to biradical **30**, which is the triplet of the photoenol, will not occur. The net result of this would be the recovery of starting material since triplet **29** would return to its ground state (**2**). Calculations (MM3) have shown that the distance between the carbonyl oxygen and the closest γ-hydrogen of **2** is 2.4 Å, a value well below the 2.7 Å limit suggested by Scheffer et al.[17] which indicated that hydrogen abstraction was not the source of this seemingly unusual result. It is well established that the geometry of $(n,\pi^*)^3$ excited states is essentially the same as it is in the ground state.[18-20]

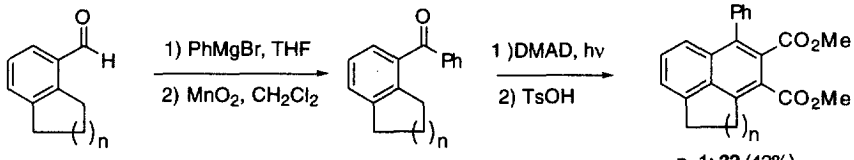


2 **29** **30**

Additionally, it was also noticed that in contrast to aldehydes **3** and **4**, autooxidation of aldehyde **2** occurred readily with significant amounts of carboxylic acid being found in the reaction mixture. Given the known effect of acid on the photoenolization process,[21] it was decided to prepare some analogs that would not be prone to the auto-oxidation problem.

The benzophenone derivatives of **31** and **32** were prepared by addition of phenylmagnesium bromide to the aldehydes, and oxidation of the resulting alcohols with manganese dioxide in methylene chloride (Scheme 5).

Scheme 5



n=1; **2**
n=2; **3**

n=1; **31** (58%)
n=2; **32** (63%)

n=1; **33** (43%)
n=2; **34** (59%)

Irradiation of ketones **31** and **32** under the same conditions described above, in the presence of one equivalent of DMAD, followed by dehydration of the intermediate dihydronaphthols, afforded naphthalene derivatives **33** and **34** in yields of 43 and 59% respectively. Although it is well known that the benzophenone triplet is a more efficient at hydrogen abstraction than the benzaldehyde triplet, the results of this trapping experiment seem to indicate that the lower yields reported for aldehyde **2** are due to acid formation and not a geometry limitation of the triplet state.

Conclusion

Bicyclic photoenols generated *via* photoenolization of bicyclic carbonyl compounds have been trapped by cycloaddition reactions with standard dieneophiles in moderate to good yields. Trapping efficiency seems independant of the size of the second ring. In the case of indane carboxaldehyde, the lower efficiency has been

ascribed to a rapid autooxidation process, and quenching of the photoenol by the generated acid. The lower endo/exo selectivity of the benzosuberane carboxaldehyde has been rationalized based on the non-planar geometry of the minimized conformation of the reactive photoenol. Currently, nanosecond time resolved laser flash photolysis studies of all aldehydes and ketones discussed in this paper are in progress which should address the effects of varying the chromophore and the geometry on triplet lifetimes and photoenolization. The results of this study will be reported in due course.

From a synthetic standpoint, the photoenolization route reported in this paper complements the thermal route presented in the previous paper.[11] The reaction conditions are much milder, being conducted at room temperature rather than in the 250-300 °C range found necessary for expulsion of SO_2 from tricylic sulfones. Additionally, *ortho*-quinodimethanes based on the indane series can be prepared via this photoenolization route. This contrasts the previously reported route based on chelotropic expulsion of SO_2 from tricyclic sulfones where the indane-based sulfone could not be prepared via standard techniques. The photoenolization route also has the advantage of giving initial cycloadducts that have a hydroxyl handle thereby allowing further chemical manipulation of the molecule.

Experimental

For comments regarding general experimental, see the experimental section of the preceding paper. Semiempirical and molecular mechanics calculations were carried out using the PM3 SCF-MO and MM3 methods respectively as implemented in Spartan version 4.04 GL (Wavefunction) running on a Silicon Graphics Indigo^2 workstation. Phenylmagnesium bromide was prepared by addition of magnesium metal to a THF solution of bromobenzene and heating at reflux. Photochemical reactions were conducted with a water-cooled Hanovia medium pressure mercury arc lamp. Acetonitrile (BDH, reagent grade) solutions of the carbonyl compounds were placed in Pyrex test tubes, sealed with rubber septa and were deoxygenated with nitrogen for 20 min prior to irradiation. After this time, the flow of nitrogen was reduced, and the samples were irradiated for the specified time 5 cm from the arc lamp.

Indane-4-carboxylic acid (10).

A solution of hydroxy-acid **8** (3.50 g, 19.7 mmol) in glacial acetic acid (20 mL) was added dropwise to a suspension of 10% Pd/C (500 mg) in glacial acetic acid (50 mL). The reaction mixture was sealed with a rubber septum, and hydrogen was bubbled through the solution for 6 h. An aliquot was worked up by filtering through a pad of Celite™, rinsing with Et_2O, then concentrating the filtrate to dryness. ^{1}H-NMR analysis of the crude product showed reaction was complete. The remainder of the reaction mixture was worked up in the same manner affording **10** as a white solid (3.20 g, 90%); **mp**: 150 °C (lit[15], mp 151-154 °C); **^{1}H-NMR** (200 MHz, $CDCl_3$) δ: 2.10 - 2.30 (m, 2H), 3.09 (t, 2H, J = 7.5 Hz), 3.46 (t, 2H, J = 7.5 Hz), 7.35 (t, 1H, J = 8.0 Hz), 7.58 (d, 1H, J = 8.0 Hz), 8.04 (d, 1H, J = 8.0 Hz) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ: 25.5, 33.1, 34.7, 126.3, 126.8, 129.4, 130.1, 146.6, 148.3, 173.5 ppm; **IR** (CH_2Cl_2): 3500, 1689 cm^{-1}; **EI-MS** m/z (%): 162 ($M^{\bullet+}$, 59.7), 117 (100); **HRMS** for $C_{10}H_{10}O_2$ Calcd: 162.06808; Found: 162.06783.

4-Hydroxymethylindane (12).

A solution of carboxylic acid **10** (3.00 g, 18.3 mmol) in tetrahydofuran (100 mL) was added dropwise to a suspension of lithium aluminium hydride (1.40 g, 37.0 mmol) in tetrahydrofuran (20 mL). After addition was complete, the reaction mixture was heated at reflux for 2 h, cooled to RT and *carefully* poured into an aqueous solution of potassium sodium tartrate (10%, 200 mL). Ethyl acetate (100 mL) was added and the mixture stirred at RT overnight. Separation of the organic phase and usual work up afforded **12** as a clear oil (2.46 g, 90%); **^{1}H-NMR** (200 MHz, $CDCl_3$) δ: 2.00 (quintet, 2H, J = 7.0 Hz), 2.70 - 2.90 (m, 4H), 4.54 (s, 2H), 7.08 (s, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ: 24.9, 30.6, 32.7, 63.4, 123.6, 124.6, 126.4, 136.3, 142.1, 144.5 ppm; **IR** (CH_2Cl_2): 3605 cm^{-1}; **EI-MS** m/z (%): 148 ($M^{\bullet+}$, 20.0), 130 (100); **HRMS** for $C_{10}H_{12}O$ Calcd: 148.08882; Found: 148.09103.

Indane-4-carboxaldehyde (2).

A mixture of benzylic alcohol **12** (2.00 g, 13.5 mmol) and activated manganese dioxide (5.00 g, 57.5 mmol) in methylene chloride (100 mL) was heated at reflux for 10 h, cooled to RT and filtered through Celite™. The filter cake was washed thoroughly with methylene chloride and the resulting clear solution was concentrated to dryness. Column chromatography (8:1 hexanes/ethyl acetate) afforded aldehyde **2** as a clear oil (1.83 g, 93%); **^{1}H-NMR** (200 MHz, $CDCl_3$) δ: 1.98 (quintet, 2H, J = 7.6 Hz), 2.77 (t, 2H, J = 7.6 Hz), 3.12 (t, 2H, J = 7.6 Hz), 7.15 (t, 1H, J = 7.3 Hz), 7.30 (d, 1H, J = 7.3 Hz), 7.45 (d, 1H, J = 7.3 Hz), 9.97 (s, 1H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ: 24.8, 31.3, 31.6, 126.3, 128.8, 129.5, 131.9, 145.8, 145.9, 192.2 ppm; **IR** (CH_2Cl_2): 1690 cm^{-1}; **EI-MS**: m/z (%): 146 ($M^{\bullet+}$, 86.8), 145 (27.0), 117 (100); **HRMS**: for $C_{10}H_{10}O$ Calcd: 146.07317; Found: 147.07645.

1,2,3,4-Tetrahydro-5-naphthoic acid (11).

Prepared following the procedure given for the preparation of **10**. In this way, **9** (4.00 g, 20.8 mmol) afforded **11** as white prisms (2.75 g, 75%); **mp**: 150 °C (lit.[15] 148-150 °C); **^{1}H-NMR** (500 MHz, $CDCl_3$) δ: 1.75 - 1.82 (m, 4H), 2.82 (t, 2H, J = 7.5 Hz), 3.12 (t, 2H, 7.5 Hz), 7.15 (t, 1H, J = 8.0 Hz), 7.25 (d, 1H, 8.0 Hz), 8.30 (d, 1H, J = 8.0 Hz) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ: 22.4, 23.1, 28.0, 30.3, 125.0, 128.7, 129.0, 134.2, 138.6, 139.9, 172.9 ppm; **IR** (CH_2Cl_2): 3495, 1690 cm^{-1}; **EI-MS** m/z (%): 176 ($M^{\bullet+}$, 71.5), 158 (81.7), 131 (100); **HRMS** for $C_{11}H_{12}O_2$: Calcd: 176.08373; Found: 176.08472.

1,2,3,4-Tetrahydro-5-hydroxymethylnaphthalene (13).

Following the same procedure as reported for **12**, **11** (2.50 g, 14.2 mmol) afforded benzylic alcohol **13** as a clear oil (2.00 g, 87%); **^{1}H-NMR** (200 MHz, $CDCl_3$) δ: 1.60 - 1.80 (m, 4H), 2.71 (t, 2H, J = 7.0 Hz), 2.85 (t, 2H, J = 7.0 Hz), 4.65 (s, 2H), 7.10 - 7.30 (m, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ: 22.5, 22.8, 25.1, 29.6, 62.7, 124.4, 125.0, 128.5, 134.6, 137.1, 138.3 ppm; **IR** (CH_2Cl_2): 3605 cm^{-1}; **EI-MS** m/z (%): 162 ($M^{\bullet+}$, 5.5), 144 (100); **HRMS** Calcd. for $C_{11}H_{14}O$: 162.10446; Found: 162.10399; **CA**: For $C_{11}H_{14}O$, Calc: C (81.44), H (8.70); Found: C (81.73), H (8.86).

1,2,3,4-Tetrahydronaphthalene-5-carboxaldehyde (3).

Prepared from benzylic alcohol **13** (2.00 g, 12.3 mmol) following the procedure given for the preparation of **2**. Column chromatography (8:1 hexanes/ethyl acetate) afforded **3** as a clear oil (1.54 g, 78%); **^{1}H-NMR** (200 MHz, $CDCl_3$) δ: 1.60 - 1.80 (m, 4H), 2.73 (t, 2H, J = 7.1 Hz), 3.10 (t, 2H, J = 7.1 Hz), 7.05 - 7.20 (m, 2H),

7.52 (d, 1H, J = 7.5 Hz), 10.15 (s, 1H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$): 21.9, 22.3, 26.0, 30.0, 124.8, 130.6, 134.0, 135.20, 138.2, 139.4, 192.9 ppm; **IR** (CH_2Cl_2): 1691 cm^{-1}; **EI-MS** m/z (%): 160 ($M^{\bullet+}$, 100), 159 (10.4), 131 (74.8); **HRMS** for $C_{11}H_{12}O$ Calcd: 160.08881; Found: 160.08961.

1-Hydroxy-9-hydroxymethylbenzosuberane (14).

A solution of benzosuberane-lactone (4.00 g, 21.3 mmol) in tetrahydofuran (50 mL) was added dropwise to a suspension of lithium aluminium hydride (0.80 g, 21.1 mmol) in tetrahydrofuran (100 mL). The resulting mixture was stirred at RT for 1 h, heated at reflux for 2 h, cooled to RT, and was poured *carefully* into an aqueous solution of potassium sodium tartrate (10%, 100 mL). Ethyl acetate (150 mL) was then added and the mixture was stirred for 10 h. Separation of the organic phase and usual work up afforded the title compound as a thick, clear oil that slowly solidified on standing. Recrystallization from diethyl ether/hexanes afforded diol **14** as a white crystalline solid (3.62 g, 89%); **^{1}H-NMR** (500 MHz, $CDCl_3$) δ: 1.45 - 1.55 (m, 1H), 1.65 - 1.72 (m, 1H), 1.75 - 1.90 (m, 2H), 2.00 - 2.09 (m, 1H), 2.10 - 2.17 (m, 1H), 2.65 - 2.75 (m, 1H), 3.18 - 3.25 (m, 1H), 4.40 (d, 1H, J = 12.5 Hz), 4.70 (d, 1H, J = 12.5 Hz), 5.25 (dd, 1H, J = 12.0, 1.0 Hz), 7.00 - 7.20 (m, 3H) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ: 24.5, 27.6, 33.4, 35.4, 65.0, 69.8, 127.5, 127.9, 131.0, 138.0, 141.7, 143.6 ppm; **IR** (CH_2Cl_2): 3596, 3392 cm^{-1}; **CA**: For $C_{12}H_{16}O_2$: Calc. C (74.97), H (8.39); Found: C (74.72), H (8.61).

9-(tert-Butyldimethylsiloxy)methyl-1-hydroxybenzosuberane (15).

A solution of *t*-butyldimethylsilyl chloride (3.02 g, 20.0 mol) in methylene chloride (50 mL) was added dropwise to a solution of diol **14** (3.50 g, 18.2 mmol), triethylamine (2.80 mL, 20.1 mmol) and 4-(dimethylamino)pyridine (200 mg) in methylene chloride (150 mL). The resulting clear solution was stirred at RT for 1h, after which time tlc analysis indicated the complete consumption of starting material. The reaction mixture was poured into water (100 mL) and the organic phase separated and subjected to standard work up. The resulting clear oil was purified by passing it through a short column of silica gel (10:1 hexanes:ethyl acetate). The resulting clear oil solidified on standing, providing the title compound **15** as a white solid (5.60 g, >95%); **mp**: 62 °C; **^{1}H-NMR** (200 MHz, $CDCl_3$) δ: 0.08 (s, 3H), 0.10 (s, 3H), 0.90 (s, 9H), 1.50 - 2.00 (m, 4H), 2.05 - 2.20 (m, 2H), 2.60 - 2.80 (m, 2H), 3.10 (br, 1H), 4.65 (d, 1H, J = 12.0 Hz), 4.90 (d, 1H, J = 12.0 Hz), 5.35 (dd, 1H, J = 3.5, 1.5 Hz), 7.05 (s, 3H) ppm; **^{13}C-NMR** (50 MHz, $CDCl_3$) δ: -5.3, -5.2, 24.6, 25.6, 25.9, 27.7, 33.1, 35.4, 65.5, 69.6, 127.1, 127.2, 130.6, 138.0, 141.9, 143.3 ppm; **IR** (CH_2Cl_2): 3599 cm^{-1}; **CA**: For $C_{18}H_{30}SiO_2$: Calcd. C (70.53), H (9.86); Found C (70.93), H (9.76).

9-(tert-Butyldimethylsiloxy)methyl-1,2-dehydrobenzosuberane (18).

A solution of alcohol **15** (2.00 g, 6.54 mmol), pyridine (1.20 mL, 14.8 mmol) and 4-(dimethylamino)pyridine (100 mg) in methylene chloride (100 mL) was stirred at RT while *para*-toluenesulfonic anhydride (2.13 g, 6.54 mmol) was added portionwise. The resulting solution was stirred at RT for 6 h, poured into water (75 mL) and the organic phase separated and subjected to standard work up. The resulting clear oil was chromatographed with hexanes, affording the title compound as a clear oil (1.60 g, 85%); **^{1}H-NMR** (200 MHz, $CDCl_3$) δ: 0.10 (s, 6H), 0.90 (s, 9H), 2.00 - 2.30 (m, 4H), 2.70 (t, 2H, J = 6.5 Hz), 4.75 (s, 2H), 6.15 (dt, 1H, J = 10.0, 6.5 Hz), 6.60 (d, 1H, J = 10.0 Hz), 7.05 - 7.20 (m, 2H), 7.38 (d, 1H, J = 7.0 Hz) ppm.

9-(tert-Butyldimethylsiloxy)methylbenzosuberane (19).

A solution of olefin **18** (1.50 g, 5.19 mmol) in methanol (50 mL) was *carefully* added dropwise to a cooled (0 °C) suspension of palladium on carbon (10%, 200 mg) in methanol (10 mL). Hydrogen was bubbled through the resulting solution for 4 h. The dark solution was then filtered through a pad of Celite™. The filter cake was then washed with diethyl ether, and the combined organic solutions evaporated to dryness. The resulting clear oil was passed through a plug of silica gel, affording the title compound as a clear oil (1.27 g, 85%); **^{1}H-NMR** (200 MHz, $CDCl_3$) δ: 0.09 (s, 6H), 0.95 (s, 9H), 1.52 - 1.70 (m, 4H), 1.75 - 1.90 (m, 2H), 2.75 - 2.90 (m, 4H), 4.70 (s, 2H), 6.95 - 7.10 (m, 2H), 7.20 (dd, 1H, J = 7.0, 1.0 Hz) ppm; **^{13}C-NMR** (50 MHz, $CDCl_3$) δ: -5.8, 18.3, 25.2, 26.0, 26.4, 27.4, 32.5, 36.1, 64.2, 125.0, 126.2, 127.3, 128.2, 131.6, 139.7 ppm; **CA**: For $C_{18}H_{30}SiO$: Calcd. C (74.42), H (10.41); Found: C (74.26), H (10.88).

9-Hydroxymethylbenzosuberane (20).

A solution of tetrabutylammonium fluoride (5.0 mL, 1.0 M in THF, 5.00 mmol) was added dropwise to a solution of silyl ether **19** (1.20 g, 3.44 mmol) in tetrahydrofuran (50 mL). The resulting solution was stirred at RT for 12 h, poured into water (50 mL) and extracted with diethyl ether (4 x 50 mL). The combined organic extracts were subjected to standard work up and the resulting clear, oily residue was purified via column chromatography (5:1 hexanes/ethyl acetate) affording the title compound as a clear colorless oil (0.60 g, 85%); **^{1}H-NMR** (200 MHz, $CDCl_3$) δ: 1.52 - 1.80 (m, 4H), 1.80 - 2.00 (m, 2H), 2.80 - 3.00 (m, 4H), 4.62 (s, 2H), 7.05 - 7.22 (m, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ: 28.2, 28.8, 30.1, 33.2, 37.0, 64.7, 126.3, 127.2, 129.6, 138.2, 142.8, 145.2 ppm; **IR** (CH_2Cl_2): 3602 cm^{-1}; **EI-MS** m/z (%): 176 ($M^{\bullet+}$, 11.9), 158 (50.2), 143 (28.9), 130 (100); **HRMS** for $C_{12}H_{16}O$ Calcd: 176.12012; Found: 176.11881.

Benzosuberan-9-carboxaldehyde (4).

A mixture of alcohol **20** (0.95 g, 5.38 mmol) and pyridinium dichromate (3.05 g, 8.11 mmol) in methylene chloride (75 mL) was stirred at RT for 12 h, after which time a 1:1 mixture of Celite™ and silica gel (2g) was added. Stirring was continued for 2 h, and the mixture was filtered through Celite™. The filter cake was washed thoroughly with diethyl ether and the combined organic solutions subjected to standard work up. The resulting yellow oil was purified via column chromatography (10:1 hexanes/ethyl acetate) affording the title compound as a clear oil (0.75 g, 80%); **^{1}H-NMR** (200 MHz, $CDCl_3$) δ: 1.50 - 1.70 (m, 4H), 1.75 - 1.95 (m, 2H), 2.75 - 2.95 (m, 2H), 3.20 - 3.40 (m, 2H), 7.15 (t, 1H, J = 7.0 Hz), 7.30 (d, 1H, J = 7.0 Hz), 7.65 (d, 1H, J = 7.0 Hz), 10.31 (s, 1H) ppm; **^{13}C-NMR** (50 MHz, $CDCl_3$) δ: 27.2, 27.5, 27.8, 32.1, 35.9, 126.0, 129.0, 133.7, 134.4, 145.6, 146.1, 192.9 ppm; **IR** (CH_2Cl_2): 1685 cm^{-1}; **EI-MS** m/z (%): 174 ($M^{\bullet+}$, 100), 173 (25.7), 145 (75.6); **HRMS** for $C_{12}H_{14}O$ Calcd.: 174.10447; Found: 174.10407.

General Experimental for the synthesis of Phenyl Ketones (31-32).

4-Benzoyl-Indane (31).

A solution of *n*-butyllithium (0.81 mL, 2.5 M in Hexanes, 2.03 mmol) was added dropwise to a cooled (-78 °C) solution of bromobenzene (320 mg, 2.04 mmol) in tetrahydrofuran (10 mL). The resulting solution was stirred at -78 °C for 30 min, after which time it was added via cannula to a cooled (-78 °C) solution of aldehyde **2** (150 mg, 1.02 mmol) in tetrahydrofuran (10 mL). The resulting solution was stirred at -78 °C for 30 min,

warmed to RT and stirred for 1 h. The pale yellow solution was then poured into a saturated aqueous solution of ammonium chloride (25 mL) and extracted with diethyl ether (5 x 15 mL). The combined organic extracts were subjected to standard work up, affording a clear oil. The intermediate alcohol was dissolved in methylene chloride (20 mL) and activated manganese dioxide was added (173 mg, 2.00 mmol). The resulting dark solution was heated at reflux for 10 h, cooled to RT and filtered through Celite™. The filter cake was washed thoroughly with methylene chloride, and resulting clear solution concentrated to dryness. The resulting pale yellow oil was chromatographed (15:1 hexanes/ethyl acetate) affording the title ketone **31** as a clear oil (132 mg, 58% from **2**); **^{1}H-NMR** (500 MHz, $CDCl_3$) δ: 2.06 (quintet, 2H, *J* = 7.5 Hz), 2.95 (t, 2H, *J* = 7.5 Hz), 3.01 (t, 2H, *J* = 7.5 Hz), 7.05 - 7.60 (m, 6H), 7.78 (dd, 2H, *J* = 7.5, 1.1 Hz) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ: 25.3, 32.6, 32.8, 125.7, 127.5, 127.8, 128.3, 130.0, 132.5, 134.4, 138.2, 144.8, 145.8, 197.8 ppm; **IR** (CH_2Cl_2): 1658 cm^{-1}; **EI-MS** m/z (%): 222 ($M^{\bullet+}$, 100), 145 (19.2), 117 (26.6); **HRMS** for $C_{16}H_{14}O$: Calcd: 222.10447; Found: 222.10422.

5-Benzoyl-1,2,3,4-tetrahydronaphthalene (32).

Using the above procedure, aldehyde **3** (150 mg, 0.95 mmol) was converted to **32** (140 mg, 63%). Ketone **32** was purified via column chromatography (25:1 hexanes/ethyl acetate) and was isolated as a clear colorless oil; **^{1}H-NMR** (200 MHz, $CDCl_3$) δ: 1.60 - 1.90 (m, 4H), 2.65 (t, 2H, *J* = 6.0 Hz), 2.85 (t, 2H, *J* = 6.0 Hz), 7.00 - 7.20 (m, 3H), 7.40 - 7.60 (m, 3H), 7.80 (d, 2H, *J* = 7.0 Hz) ppm; **^{13}C-NMR** (50 MHz, $CDCl_3$) δ: 22.6, 22.9, 27.1, 29.8, 124.7, 125.3, 128.4, 130.0, 131.0, 133.1, 135.3, 137.6, 138.0, 136.8, 199.1 ppm; **IR** (CH_2Cl_2): 1675 cm^{-1}; **EI-MS** m/z (%): 236 ($M^{\bullet+}$, 100), 159 (7.2), 131 (15.9); **HRMS** for $C_{17}H_{16}O$: Calcd. 236.12011; Found: 236.11904.

General Procedure for the Generation and Trapping of Photoenols

A solution of the appropriate aldehyde or ketone (50-100 mg) in CH_3CN (10 mL) and the desired dienophile (2 equivalents) was placed in a Pyrex test tube and was sealed with a rubber septum. The solution was deoxygenated with oxygen-free nitrogen for 20 min, after which time the flow of nitrogen was reduced, the test tube was placed 5 cm from a water-cooled Hanovi medium pressure mercury arc lamp and the sample irradiated for 12h. The solvent was evaporated and the product purified by column chromatography. In the cases where dimethylacetylene dicarboxylate was used as the dienophile, the reaction mixture was transferred to a round-bottom flask, a crystal of *para*-toluenesulfonic acid added and the resulting mixture was heated at reflux for 1h. The solvent was evaporated and the product isolated by column chromatography.

Cycloadduct 22.

Using the general procedure, aldehyde **3** (90 mg, 0.56 mmol) was converted into a 15:1 mixture of endo:exo cycloadducts, which was purified via column chromatography (3:1 hexanes/ethyl acetate). Cycloadduct **22** was obtained as a white solid (120 mg, 70%); **mp**: 167 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ: 1.40 - 1.50 (m, 1H), 1.70 - 1.80 (m, 1H), 1.90 - 1.95 (m, 2H), 2.70 - 2.85 (m, 3H), 3.22 (dd, 2H, *J* = 10.0, 3.0 Hz), 3.75 (s, 3H), 3.77 (s, 3H), 5.13 (d, 1H, *J* = 3H), 7.05 - 7.15 (m, 1H), 7.20 - 7.30 (m, 2H) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ: 22.1, 27.6, 28.9, 29.6, 43.7, 49.4, 51.9, 52.2, 68.2, 126.8, 126.9, 129.3, 134.1, 135.4, 137.2, 172.6, 175.5 ppm; **IR** (CH_2Cl_2): 3550, 1734 cm^{-1}; **CI-MS** m/z (%): 305 ($M^{\bullet+}$+1); **HRMS** for $C_{17}H_{18}O_4$ [($M^{\bullet+}$)-H_2O]: Calcd. 286.12051; Found: 286.12103.

Cycloadduct 23.

Using the general procedure, aldehyde **4** (50 mg, 0.29 mmol) was converted into a 3:1 mixture of endo:exo cycloadducts, which was purified via column chromatography (3:1 hexanes/ethyl acetate). Cycloadduct **23** was obtained as a clear oil (35 mg, 40%); **^{1}H-NMR** (500 MHz, $CDCl_3$) δ: 1.20 - 1.30 (m, 1H), 1.35 - 1.45 (m, 1H), 1.58 - 1.68 (m, 1H), 1.85 - 1.90 (m, 1H), 1.95 - 2.00 (m, 1H), 2.00 - 2.10 (m, 1H), 2.65 - 2.75 (m, 2H), 2.80 - 2.90 (m, 1H), 3.05 - 3.2 (m, 2H), 3.74 (s, 3H), 3.76 (s, 3H), 5.00 (d, 1H, *J* = 3.0 Hz), 7.05 - 7.15 (m, 3H) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ: 27.3, 31.7, 36.3, 36.6, 41.0, 44.6, 47.0, 52.2, 52.3, 69.1, 126.4, 127.7, 130.6, 135.1, 139.1, 143.4, 173.7, 176.0 ppm; **IR** (CH_2Cl_2): 3589, 1733 cm^{-1}; **EI-MS** m/z (%): 318 ($M^{\bullet+}$, 1.5), 300 (5.9), 240 (100); **HRMS** for $C_{18}H_{22}O_5$ Calcd.318.14672; Found: 318.14676.

Cycloadduct 25.

Using the general procedure, aldehyde **4** (90 mg, 0.56 mmol) was converted into cycloadduct **25** which was purified via column chromatography (5:1 hexanes/ethyl acetate). Cycloadduct **25** was obtained as a pale yellow solid (70 mg, 44%); **mp**: 78 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ: 2.03 (quintet, 2H, *J* = 8.0 Hz), 3.05 (t, 2H, *J* = 8.0 Hz), 3.90 (t, 2H, *J* = 8.0 Hz), 3.92 (s, 3H), 3.96 (s, 3H), 7.35 (dd, 1H, *J* = 8.0, 1.0 Hz), 7.45 (t, 1H, *J* = 8.0 Hz), 7.74 (dd, 1H, *J* = 8.0, 1.0 Hz), 8.38 (s, 1H) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ: 22.5, 28.2, 30.7, 52.5, 52.5, 122.1, 124.4, 127.2, 127.2, 127.4, 129.8, 131.4, 132.6, 134.6, 137.2, 166.6, 170.2 ppm; **IR** (CH_2Cl_2): 1727 cm^{-1}; **EI-MS** m/z (%): 284 ($M^{\bullet+}$, 5.6), 225 (36.8), 165 (13.5), 113 (100); **HRMS** for $C_{17}H_{16}O_4$ Calcd. 284.10486; Found: 284.10503.

Cycloadduct 26.

Using the general procedure, aldehyde **4** (50 mg, 0.29 mmol) was converted into cycloadduct **26** which was purified via column chromatography (5:1 hexanes/ethyl acetate). Cycloadduct **26** was obtained as a pale yellow solid (67 mg, 78%); **mp**: 138 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ: 1.80 - 2.00 (m, 4H), 3.00 - 3.10 (m, 2H), 3.20 - 3.40 (m, 2H), 3.90 (s, 3H), 3.95 (s, 3H), 7.20 - 7.40 (m, 2H), 7.71 (dd, 1H, *J* = 8.0, 1.0 Hz), 8.35 (s, 1H) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ: 26.1, 26.2, 29.9, 34.3, 52.4, 52.5, 124.1, 126.9, 128.3, 130.4, 130.7, 131.1, 133.9, 135.6, 138.8, 142.1, 166.4, 170.6 ppm; **IR** (CH_2Cl_2): 1717 cm^{-1}; **EI-MS** m/z (%): 298 ($M^{\bullet+}$, 20.6), 266 (100); **HRMS** for $C_{18}H_{18}O_4$: Calcd. 298.12051; Found: 298.12056.

Cycloadduct 28.

Using the general procedure, aldehyde **3** (90 mg, 0.56 mmol) was converted into cycloadduct **28** which was purified via column chromatography (10:1 hexanes/ethyl acetate). Cycloadduct **28** was obtained as a pale yellow oil (83 mg, 61%); **^{1}H-NMR** (500 MHz, $CDCl_3$) δ: 1.42 (t, 3H, *J* = 7.5 Hz), 2.06 (quintet, 2H, *J* = 7.5 Hz), 3.08 (t, 2H, *J* = 7.5 Hz), 3.11 (t, 2H, *J* = 7.5 Hz), 4.45 (q, 2H, *J* = 7.5 Hz), 7.20 (dd, 1H, *J* = 8.0, 1.0 Hz), 7.40 (t, 1H, *J* = 8.0 Hz), 7.76 (dd, 1H, *J* = 8.0, 1.0 Hz), 7.80 (d, 1H, *J* = 1.0 Hz), 8.40 (d, 1H, *J* = 1.0 Hz) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ: 14.4, 23.0, 31.2, 61.0, 123.0, 126.1, 126.2, 127.1, 127.4, 128.9, 132.2, 132.9, 136.5, 136.8, 167.1 ppm; **IR** (CH_2Cl_2): 1711 cm^{-1}; **EI-MS** m/z (%): 240 ($M^{\bullet+}$, 100), 195 (49.5), 167 (76.6); **HRMS** for $C_{16}H_{16}O_2$ Calcd. 240.11503; Found: 240.11391.

Cycloadduct 33.

Using the general procedure, ketone **31** (50 mg, 0.23 mmol) was converted into cycloadduct **33** which was purified via column chromatography (5:1 hexanes/ethyl acetate). Cycloadduct **33** was obtained as a pale yellow solid (33 mg, 43%); **mp**: 150 °C; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ: 3.44 (t, 2H, *J* = 7.5 Hz), 3.56 (s, 3H), 3.70 (t, 2H, *J* = 7.5 Hz), 3.92 (s, 3H), 7.20 - 7.60 (m, 8H) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ: 30.5, 32.7, 52.0, 52.1, 119.1, 121.3, 122.1, 127.8, 128.0, 130.1, 130.8, 132.2, 132.8, 135.2, 136.5, 138.8, 147.8, 151.1, 166.9, 169.9 ppm; **IR** (CH_2Cl_2): 1725 cm^{-1}; **EI-MS** m/z (%): 346 ($M^{\bullet+}$, 39.7), 314 (100), 228 (35.5); **HRMS** for $C_{22}H_{18}O_4$: Calcd: 346.12051; Found: 346.111975.

Cycloadduct 34.

Using the general procedure, ketone **32** (75 mg, 0.32 mmol) was converted into cycloadduct **34** which was purified via column chromatography (10:1 hexanes/ethyl acetate). Cycloadduct **34** was obtained as a pale yellow oil (68 mg, 59%); **^{1}H-NMR** (500 MHz, $CDCl_3$) δ: 2.08 (quintet, 2H, *J* = 7.5 Hz), 3.12 (t, 2H, *J* = 7.5 Hz), 3.23 (t, 2H, *J* = 7.5 Hz), 3.47 (s, 3H), 3.89 (s, 3H), 7.20 - 7.40 (m, 8H) ppm; **^{13}C-NMR** (125 MHz, $CDCl_3$) δ: 22.8, 29.2, 31.2, 52.0, 52.4, 125.6, 125.9, 126.2, 127.4, 127.6, 127.9, 128.7, 129.6, 130.0, 130.2, 133.1, 136.0, 137.5, 138.1, 168.9, 169.1 ppm; **IR** (CH_2Cl_2): 1730 cm^{-1}; **EI-MS** m/z (%): 360 ($M^{\bullet+}$, 16.0), 328 (100); **HRMS** for $C_{23}H_{20}O_4$ Calcd: 360.13616; Found: 360.13705.

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